RESTRICTED ROTATION IN SEVERAL DISUBSTITUTED DIAMINOMESITYLENES

BY

RICHARD GOLDEN CHASE

A.B., Dartmouth College, 1938
A.M., Dartmouth College, 1940

AN ABSTRACT OF A THESIS

SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS
FOR THE DEGREE OF DOCTOR OF PHILOSOPHY IN
CHEMISTRY IN THE GRADUATE SCHOOL OF
THE UNIVERSITY OF ILLINOIS, 1943

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INTRODUCTION

Molecules of the type CH_2XCH_2X have been shown to exhibit rotational isomerism.[1] It has not been possible to isolate two forms of these molecules since the energy of conversion from one form to the other is small. If however, the groups surrounding a carbon-to-carbon single bond occupy a sufficiently large volume, a spatial deformation of the groups would be necessary in order to convert one isomer into the other. In molecules of the latter type, considerable stability of the isomers could be expected.

Enantiomorphic forms of molecules in which rotation about a carbon-to-carbon single bond is restricted by neighboring spatial groups have been isolated by Christie and Kenner.[2] The same phenomena has been shown to exist for the carbon-to-nitrogen bond by Mills and Elliott,[3] who isolated the d and l forms of N-benzenesulfonyl-8-nitro-1-naphthylglycine. A compound with two centers of restricted rotation should exhibit geometric isomerism. Both the cis and trans forms of 3,6-di-(2,4-dimethylphenyl)-2,5-dibromodihydroquinone, which contains two centers of restricted rotation, were isolated by Browning and Adams.[4]

The object of this research was to synthesize several disubstituted diaminomesitylene derivatives which should contain two hindered carbon-to-nitrogen bonds, and to determine whether stable isomers of the cis-trans type occur.

DISCUSSION OF RESULTS

Dinitromesitylene, which was produced by the direct nitration of mesitylene, was reduced to diaminomesitylene by catalytic hydrogenation. This compound was converted to N,N′-diacetyl-N,N′-dimethyldiaminomesitylene, both by meth-

ylation using dimethyl sulfate with consequent acetylation in pyridine and acetic anhydride mixture, and by acetylation followed by methylation with dimethyl sulfate or methyl iodide. One form only of N,N′-diacetyl-N,N′-dimethyldiaminomesitylene was isolated. The intermediate products were isolated and identified in each series of reactions.

The treatment of N,N′-dimethyldiaminomesitylene with sodium nitrate and hydrochloric acid produced a brown oil distilling at 118-120°/3mm. and a white solid melting from 121 to 122.° These compounds were apparently isomeric forms of N,N′-dinitroso-N,N′-dimethlydiaminomesitylene although the oil has not been identified conclusively.

Trinitromesitylene was produced according to the method of Blanksma[5] and reduced to diaminonitromesitylene using a modification of the procedure of Fittig.[6] The latter compound was methylated and acetylated. Only one form of N,N′-diacetyl-N,N′-dimethyldiaminonitromesitylene was isolated. The same series of reactions starting with bromomesitylene produced only one form of N,N′-diacetyl-N,N′-dimethyldiaminobromomesitylene.

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VITA

The writer was born in New York City on October 5, 1916. He received his elementary education in the public schools of Washington, Harrisburg, and Albany. He attended the Albany Academy from which he graduated in 1934. In the fall of the same year, he entered Dartmouth College from which he received the degree of Bachelor of Arts in Chemistry in June, 1938, and the degree of Master of Arts in Chemistry in June 1940. From September 1938 until June 1940 he was Assistant in Chemistry at Dartmouth College. He held a similar position in his subsequent work in the University of Illinois during the period from September 1940 to October 1943.

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